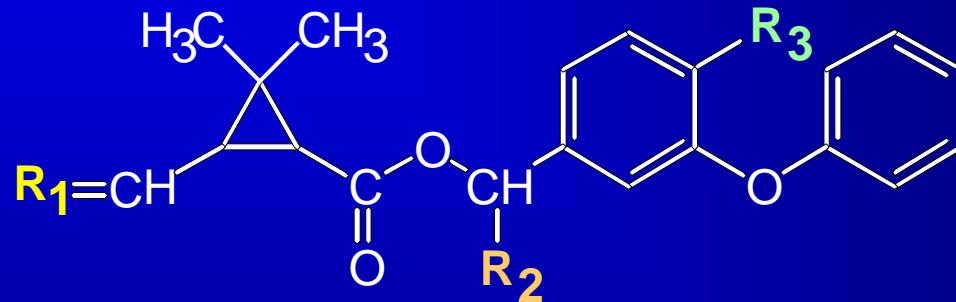


Synthetic Pyrethroids and California Surface Water

Use patterns, properties, unique aspects



Frank Spurlock

Environmental Monitoring
California Department of Pesticide Regulation

I. Introduction: California Surface Water & Pesticides

II. California Ag and Urban Insecticides

use trends

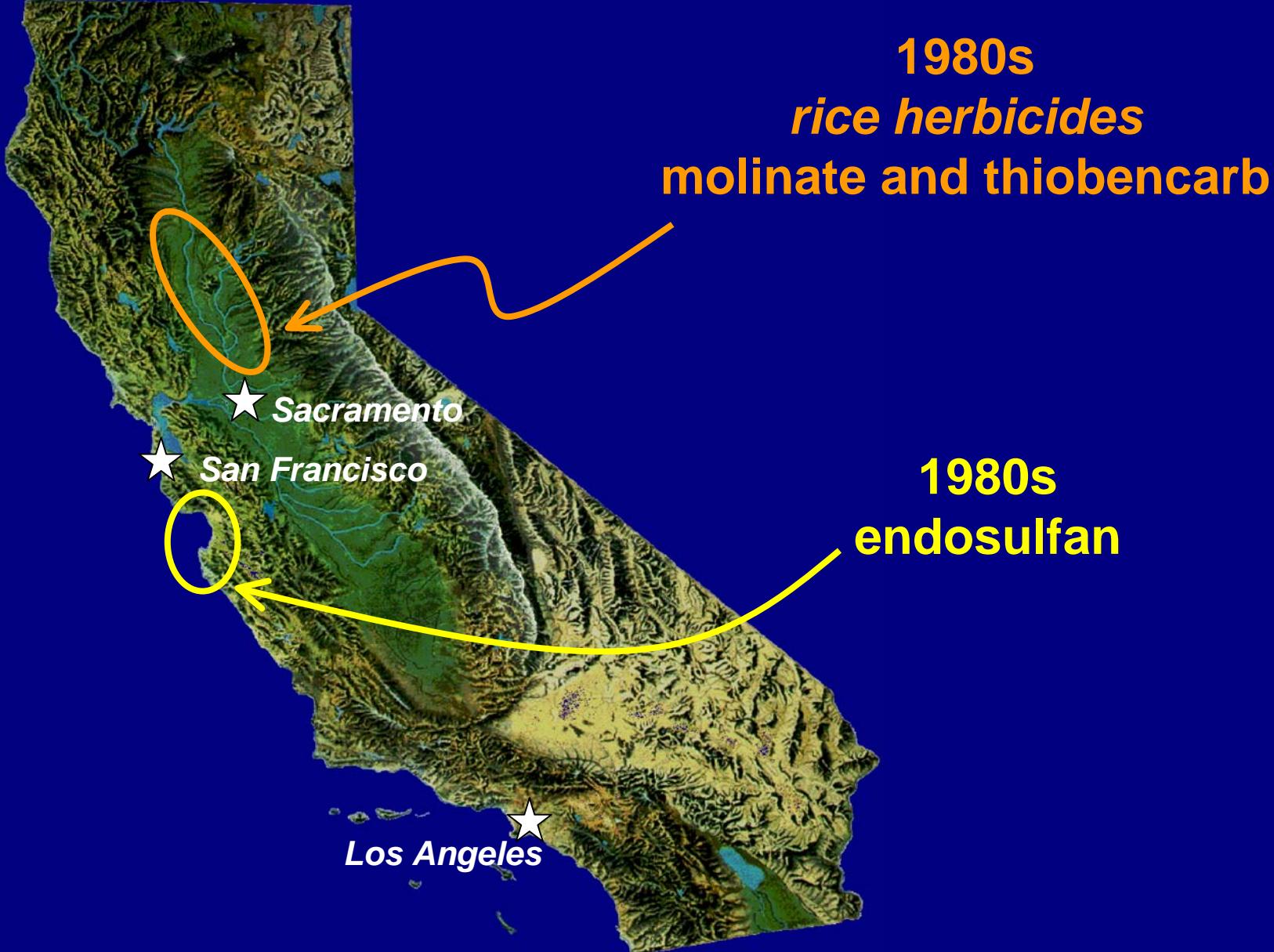
pyrethroid active ingredients

pyrethroid use patterns

III. Pyrethroid Environmental Fate Overview

IV. Pyrethroid Aquatic Risk Assessment Issues

Pesticides and water quality



Pesticides and water quality

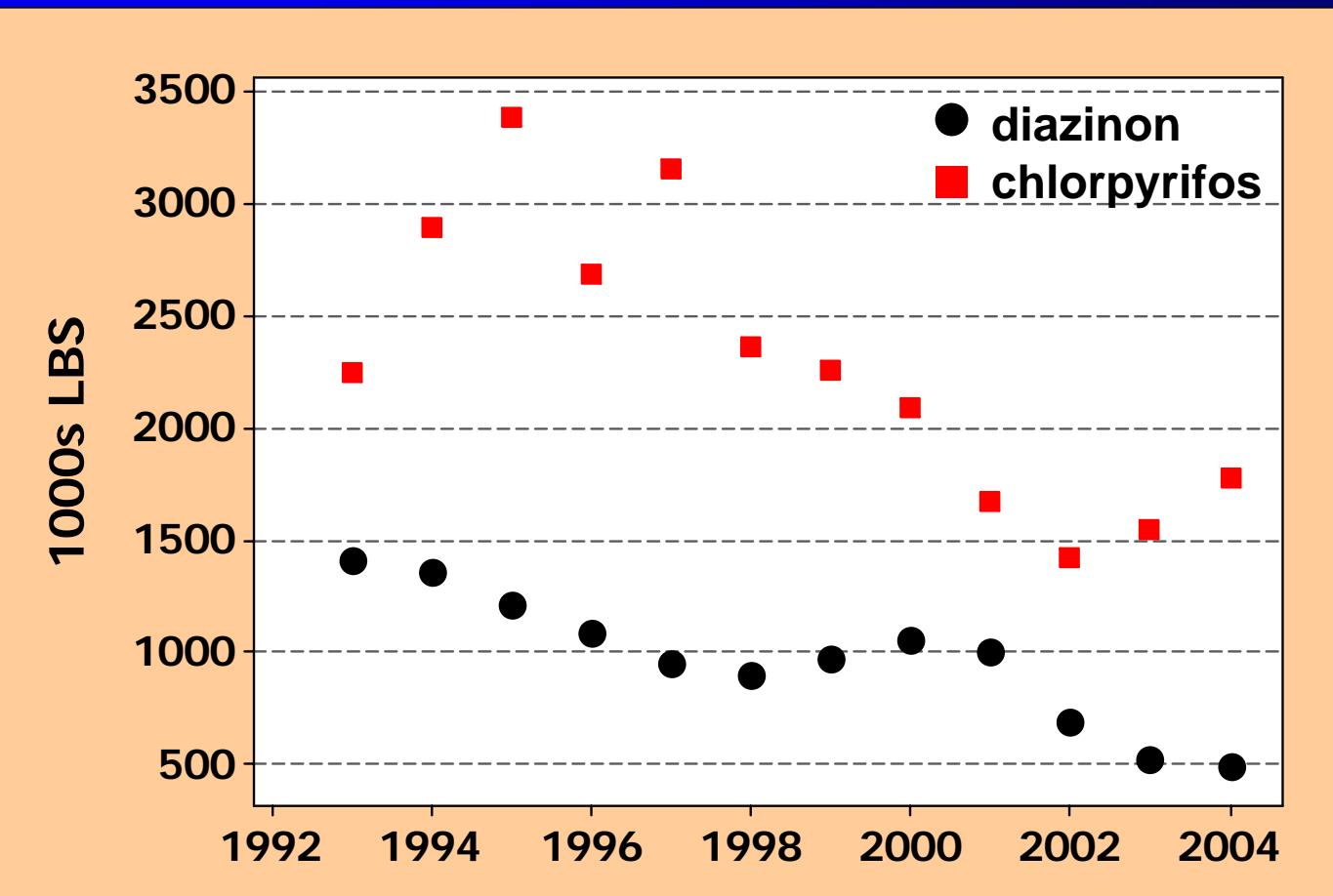


1990s – present
organophosphates, e.g.
diazinon and chlorpyrifos

→ detections and toxicity in both
ag and urban waterways

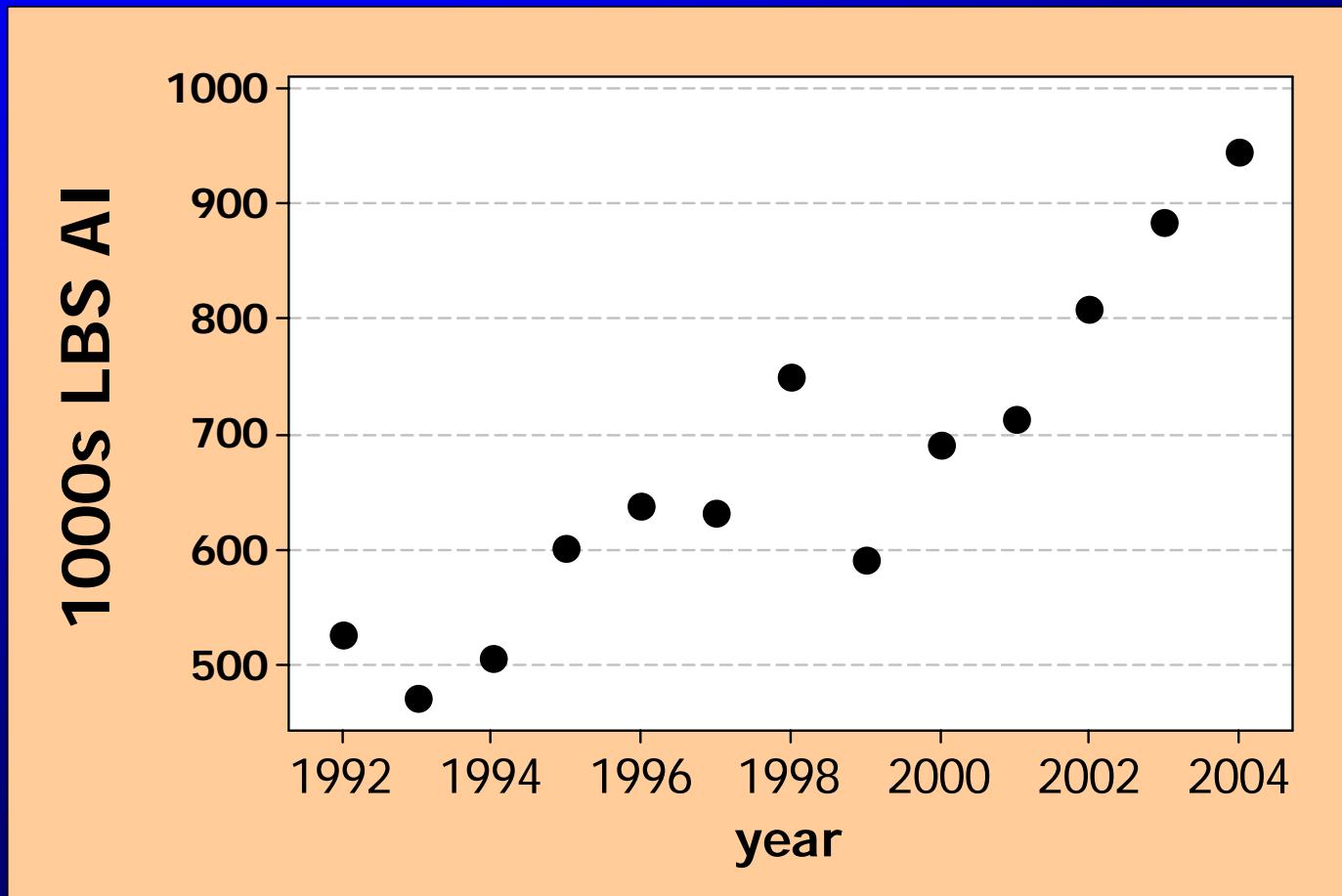
Diazinon and chlorpyrifos use trends

production ag and commercial structural



Synthetic pyrethroid use trend - Σ 25 AIs

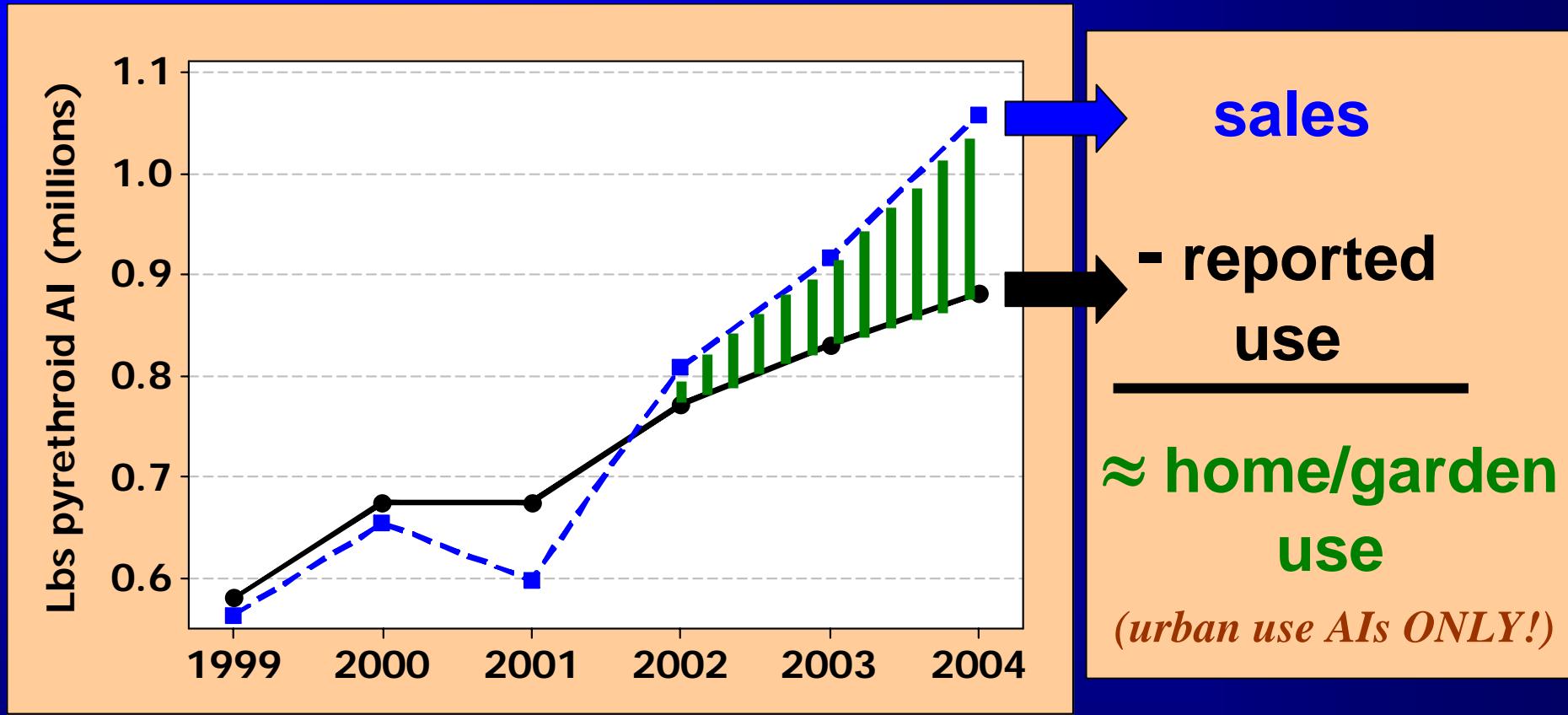
production ag and commercial structural



2004 TOP 7
permethrin
cypermethrin
bifenthrin
cyfluthrin
fenpropathrin
 λ -cyhalothrin
esfenvalerate

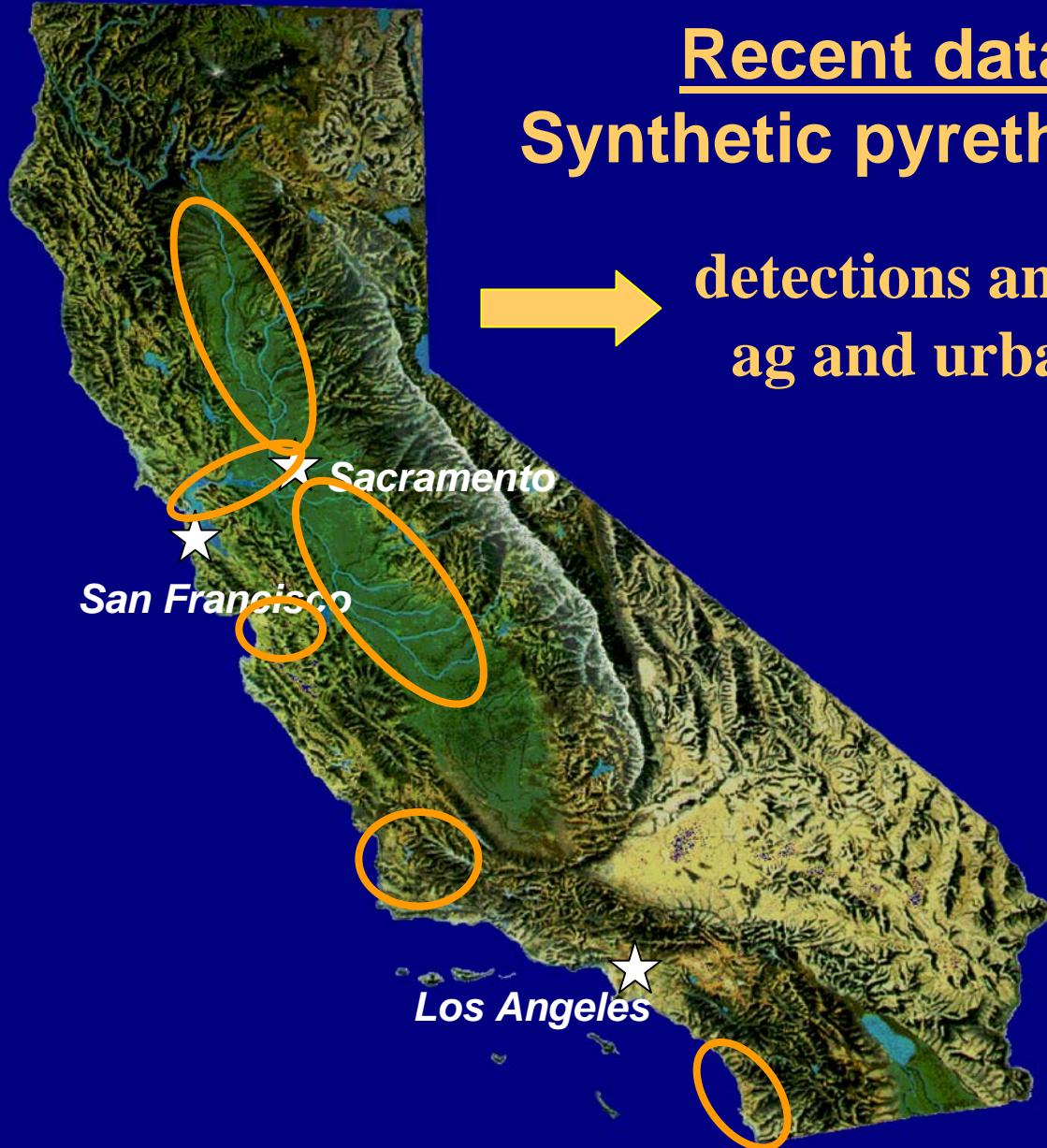
>30000 lbs
use in 2004

Inferring home & garden use trend from sales and reported (ag + structural) use



OP urban use phaseout

Pesticides and water quality



Recent data Synthetic pyrethroids

→ detections and bioassay toxicity in
ag and urban aquatic sediments

bifenthrin
cypermethrin
cyfluthrin
 λ - cyhalothrin
permethrin
esfenvalerate
fenpropathrin
deltamethrin

Current California registrations

- 25 synthetic pyrethroids (including isomerically-enriched mixtures)

ALLETHRIN	DELTAMETHRIN
S-BIOALLETHRIN	ESFENVALERATE
D-TRANS ALLETHRIN	ETOGENPROX
D-ALLETHRIN	FENPROPATHRIN
ESBIOTHRIN	IMIPROTHRIN
BIFENTHRIN	PERMETHRIN
CYFLUTHRIN	PHENOTHRIN
BETA-CYFLUTHRIN	PRALLETHRIN
CYPERMETHRIN	RESMETHRIN
(S)-CYPERMETHRIN	TAU-FLUVALINATE
CYPHENOTHRIN	TETRAMETHRIN
LAMBDA CYHALOTHRIN	TRALOMETHRIN
GAMMA CYHALOTHRIN	

Current California registrations

- 25 active ingredients registered (including isomerically-enriched mixtures)
- 1255 synthetic pyrethroid products registered, 197 registrants (1/2006)

Current California registrations

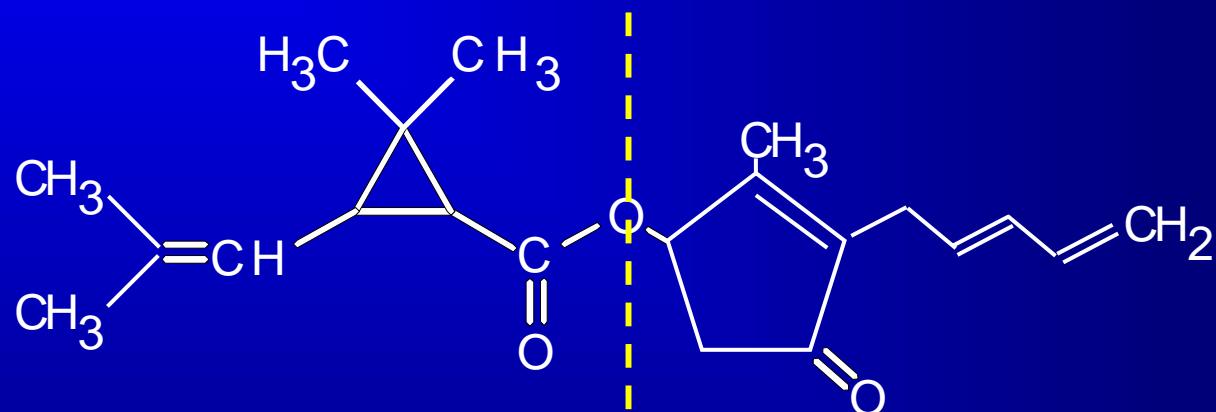
- 25 active ingredients registered (including isomerically-enriched mixtures)
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- > 40% of ALL *insecticide products*

Current California registrations

- 25 active ingredients registered (including isomerically-enriched mixtures)
- 1255 synthetic pyrethroid products registered, 197 registrants (1/2006)
- > 40 % of ***ALL insecticide products***
- Total 2004 sales: ~ 1.3M lbs AI, > \$160M

Use patterns and characteristics

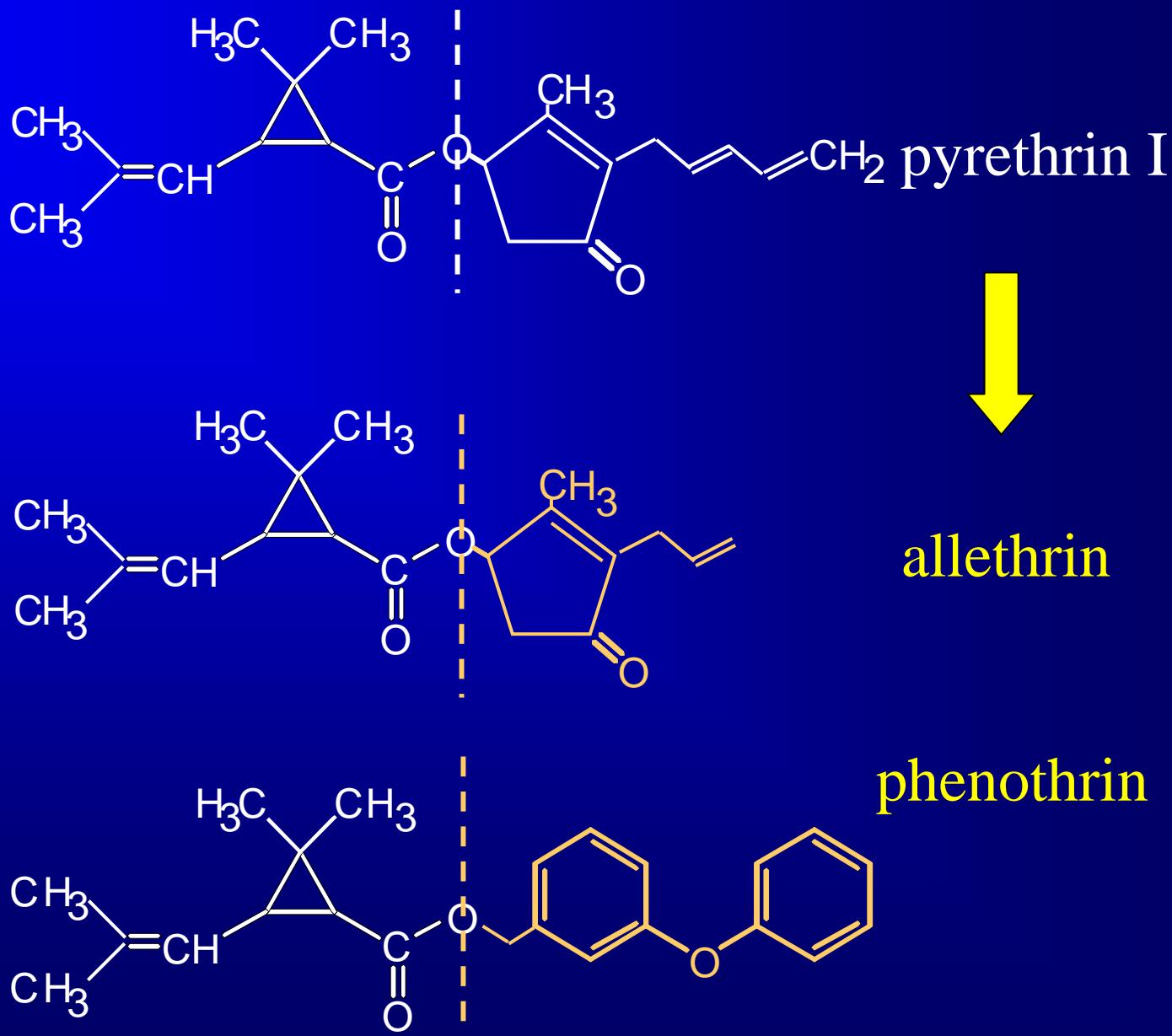
pyrethrin I



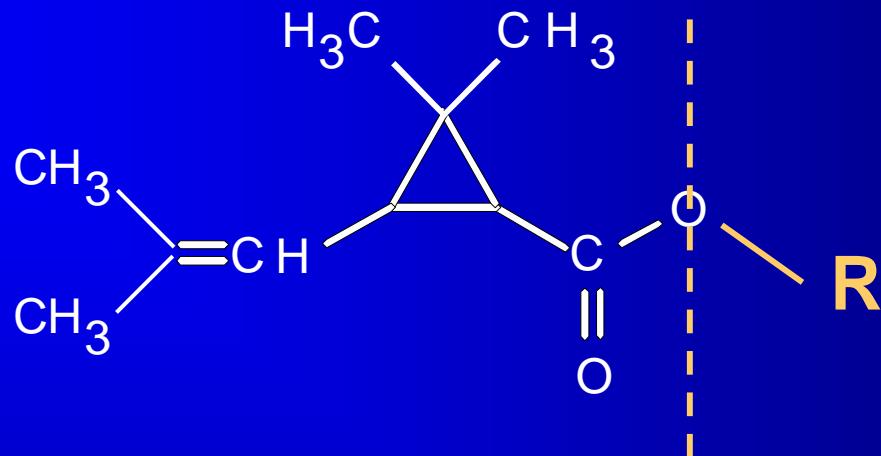
chrysanthemic
acid

pyrethrone
(alcohol)

Early syntheses: alcohol substitutions

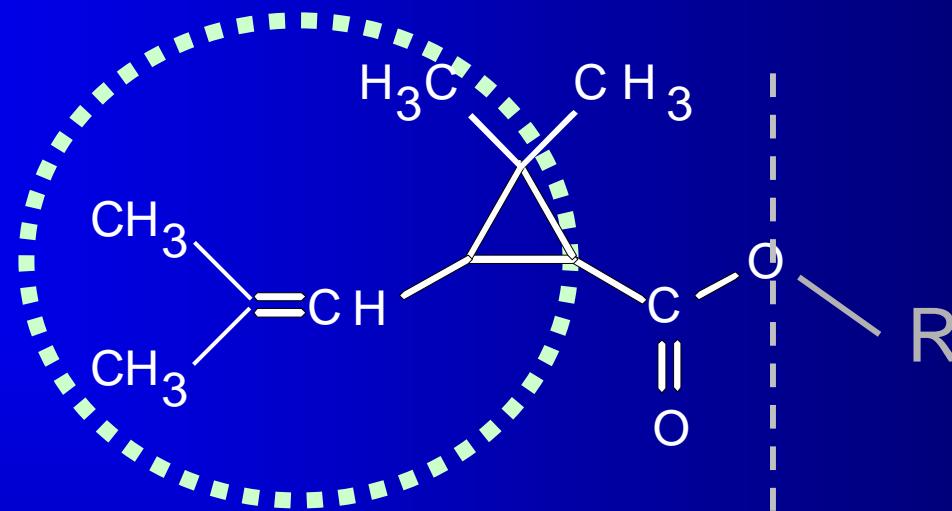


Early syntheses: alcohol substitutions



CA registered Als
allethrin
cyphenothrin
imiprothrin
prallethrin
phenothrin
resmethrin
tetramethrin

Early syntheses: alcohol substitutions



* PHOTOLABILE *

$t_{1/2} \sim$ hours

Nonag uses:

aerosol ant/roach sprays
fly/wasp sprays
indoor foggers
carpet/upholstery sprays
pet products
commercial/institutional
crack/crevice

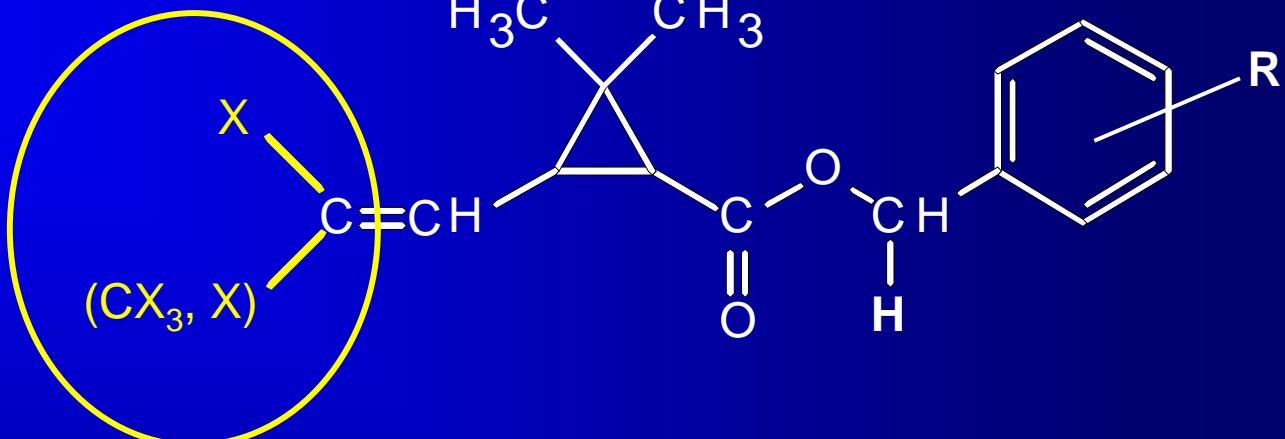
CA registered Als

allethrins
cyphenothrin
imiprothrin
prallethrin
phenothrin
resmethrin
tetramethrin

~ 8%
CA
sales

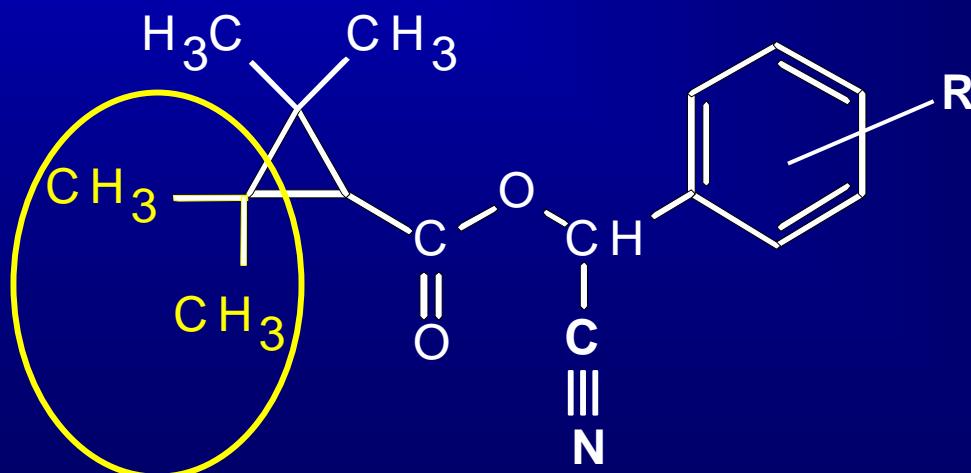
Later syntheses

vinylic halogens
 (CX_3, X)

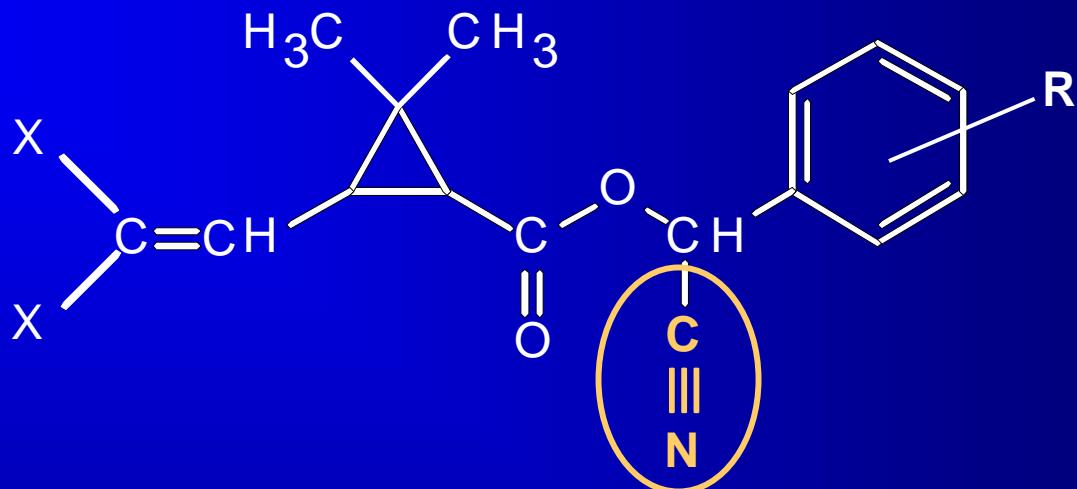


**improved
photostability**

tetra-alkylcyclopropane
ester

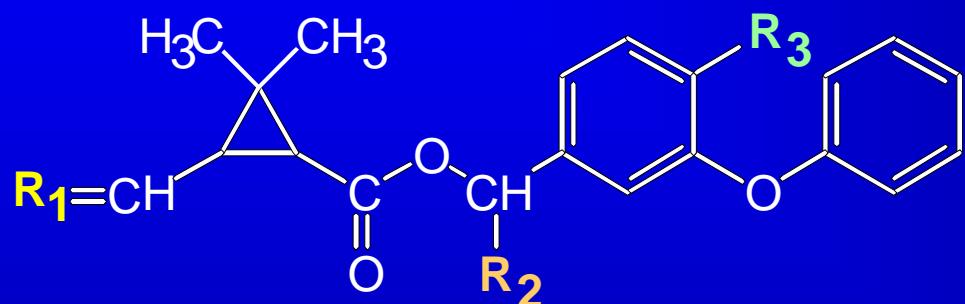


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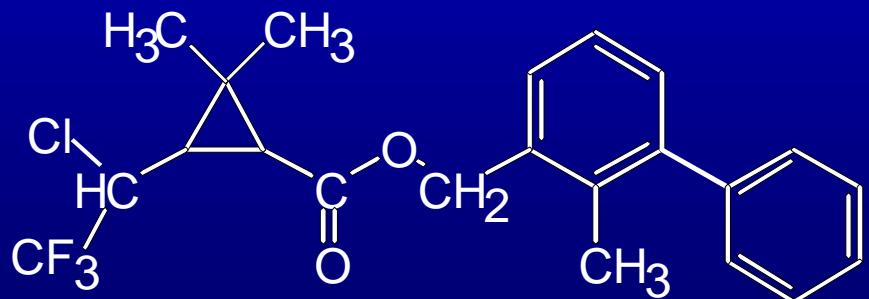


α -cyano substitution
marked increase in
insecticidal activity
(“type II” pyrethroids)

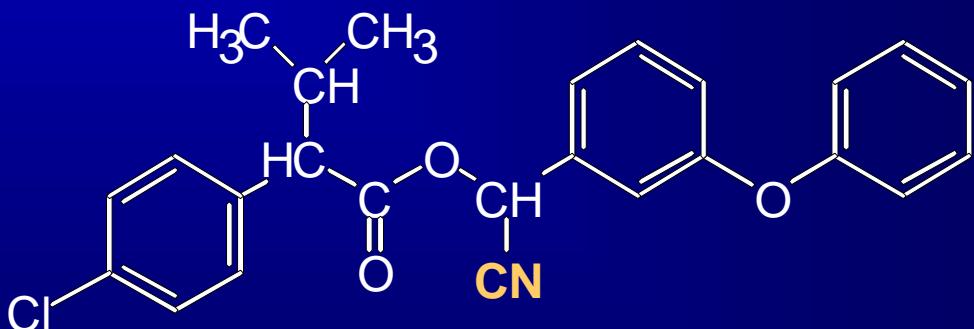
Examples of photo-stable type I and II pyrethroids



R_1	R_2	R_3	
CCl_2	CN	F	cyfluthrin
CCl_2	CN	H	cypromethrin
CClCF_3	CN	H	cyhalothrin
CCl_2	H	H	permethrin



bifenthrin



fenvalerate

Photo-stable pyrethroids

- Primary focus of pyrethroid water quality concerns

Photo-stable pyrethroids

- Primary focus of pyrethroid water quality concerns
- > 90% CA pyrethroid use
 - Agricultural , numerous crops
 - Nursery, turf and sod
 - Institutional/commercial
 - Pet products and shampoos
 - Animal husbandry premises
 - horses, livestock, barns
 - Landscape maintenance -
 - golf courses, parks, buildings
 - Structural
 - building exteriors, crack & crevice
 - termite applications
 - Home and garden
 - lawns, ornamental flowers, indoor uses

Photo-stable pyrethroids

- Primary focus of pyrethroid water quality concerns
- Broad range of uses
- General Use Categories & 2004 amount:

**Agricultural
(~ 300k lbs)**

permethrin (140k)
fenpropathrin (40k)
esfenvalerate (30k)

**Comm'l structural &
landscape maint.
(~ 640k lbs)**

permethrin (320k)
cypermethrin (200k)

**Est.remaining
urban uses
(~ 100k lbs)**

bifenthrin (50k)
esfenvalerate (30k)
permethrin (20k)

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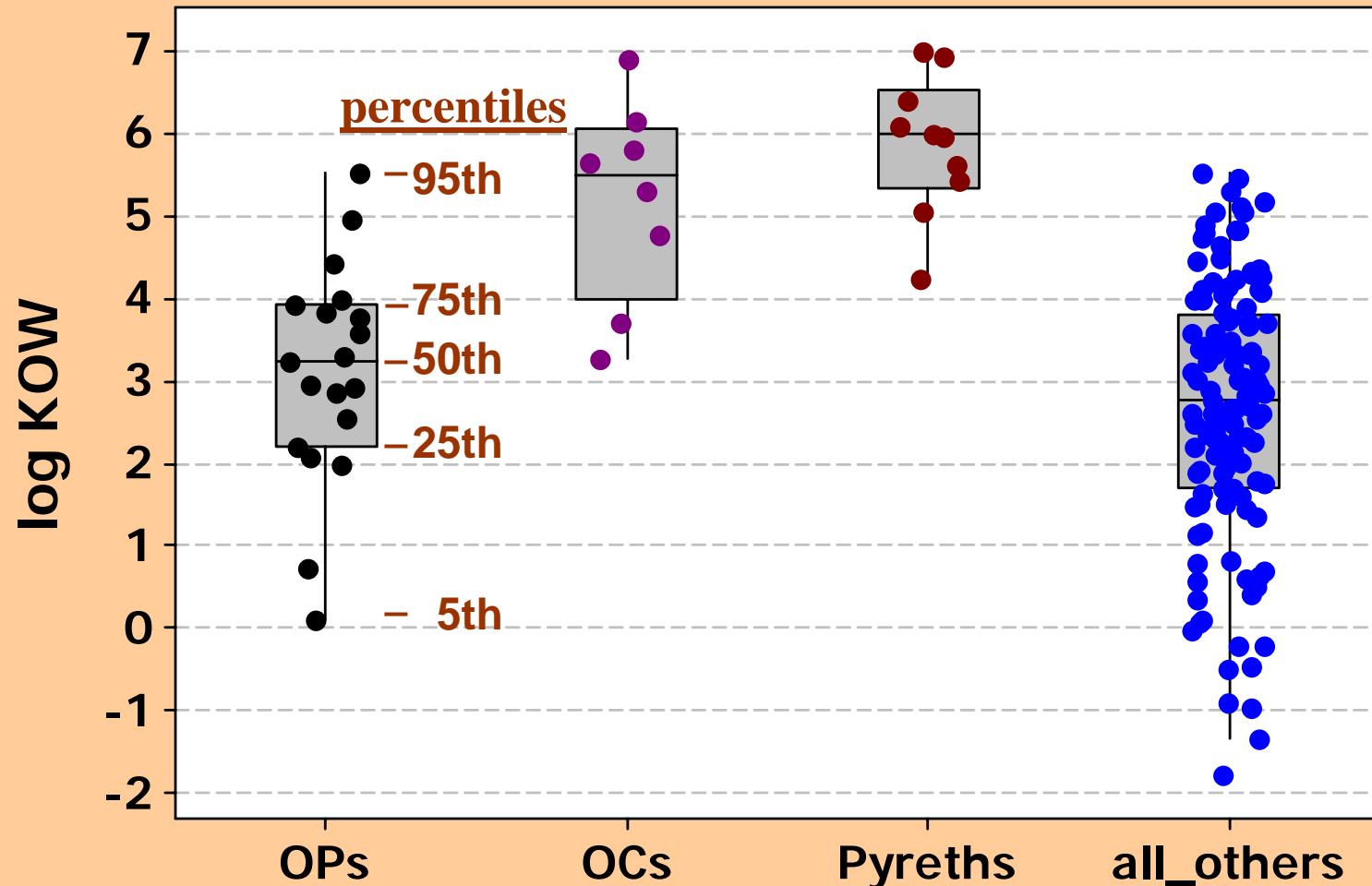
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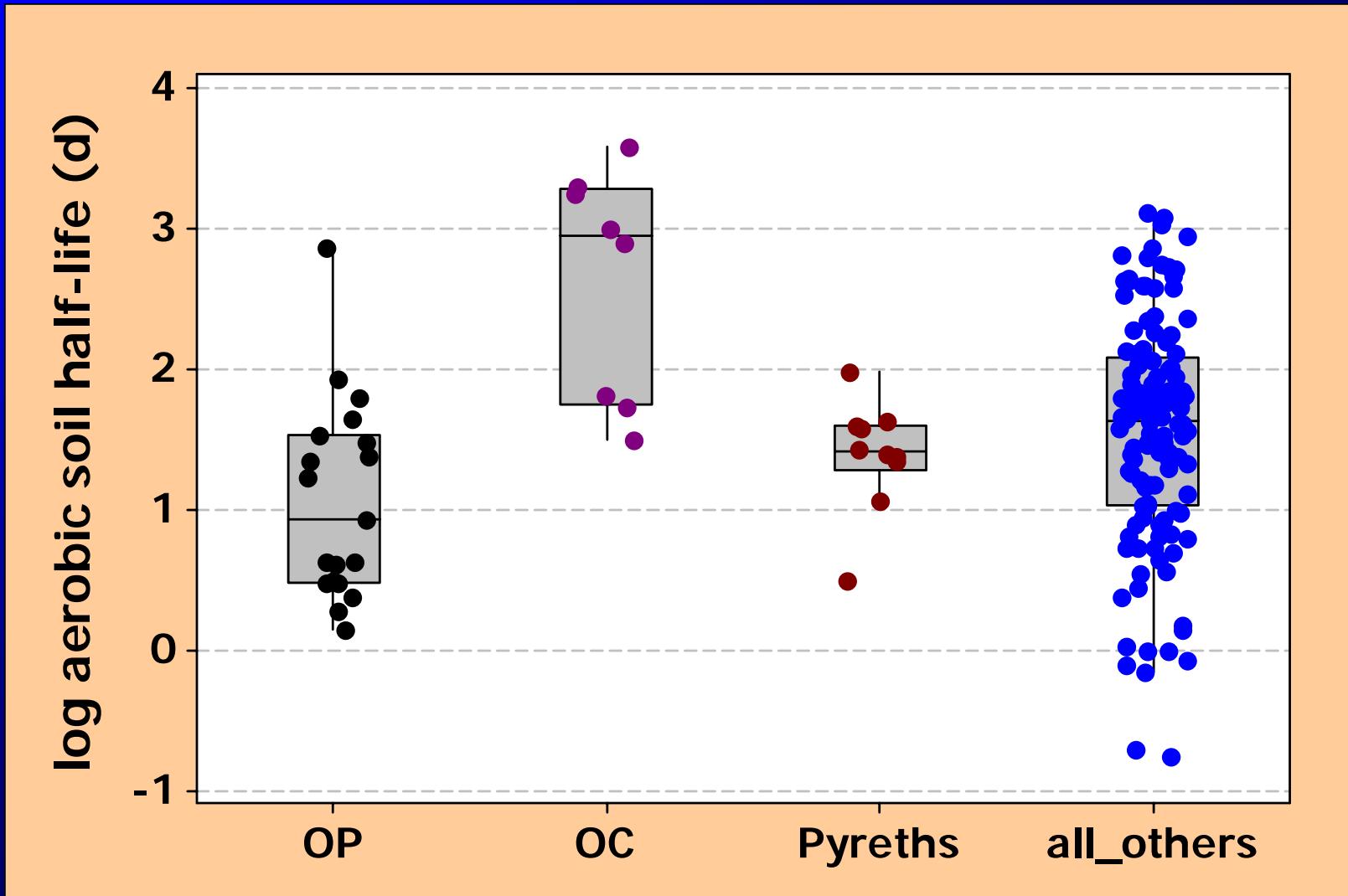
permethrin: 40 - 50% of all pyrethroid sales

Pyrethroid properties

hydrophobicity



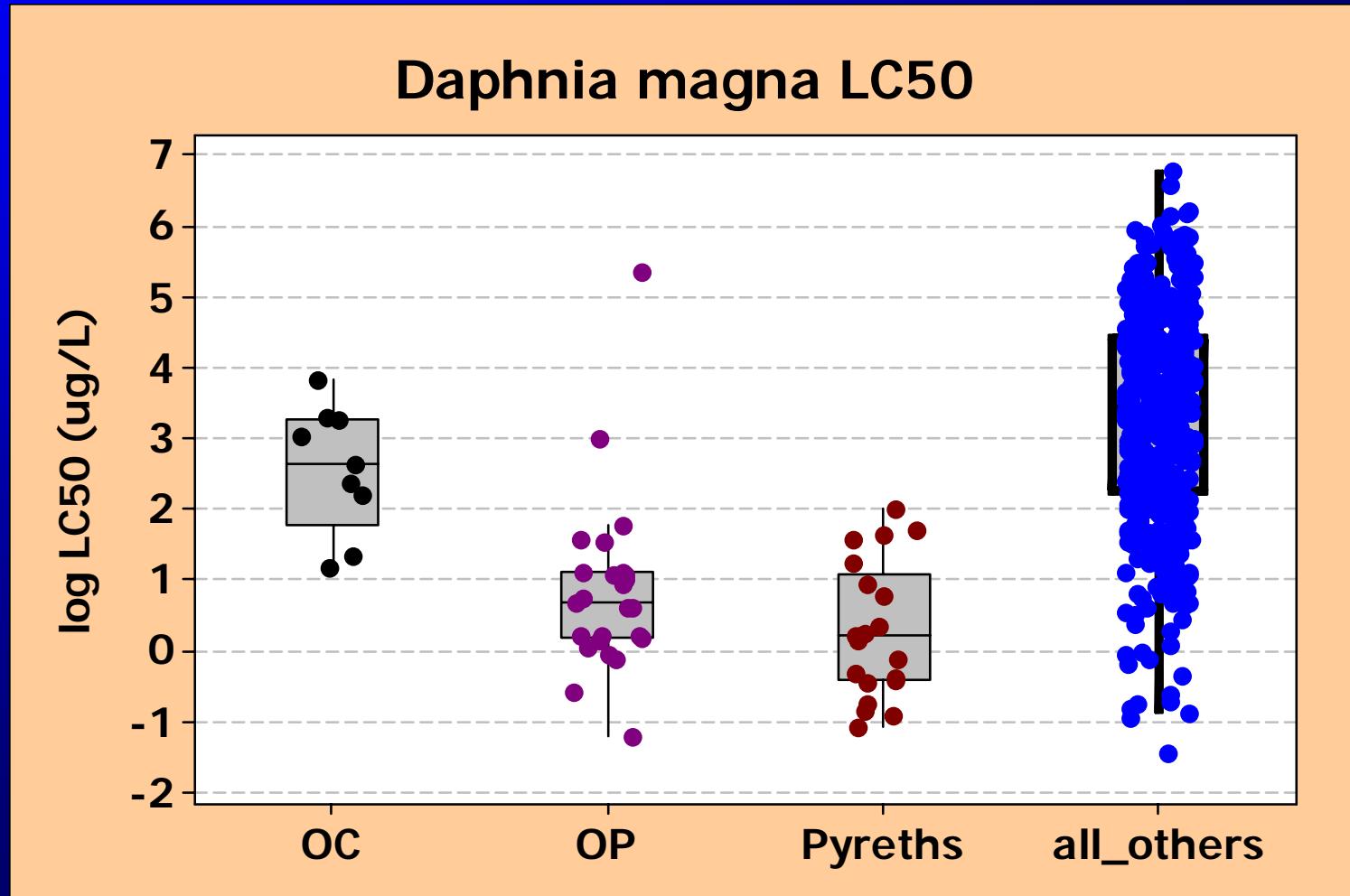
Pyrethroid properties soil persistence



Pyrethroid properties

relative potential acute aquatic toxicity

(“water-only” data)



Pyrethroid aquatic risk assessment issues

• Pyrethroids are highly toxic to aquatic life

• Pyrethroids are persistent in the environment

• Pyrethroids bioaccumulate in aquatic organisms

• Pyrethroids are mobile in the environment

• Pyrethroids are photolabile in the environment

• Pyrethroids are bioconcentrated by phytoplankton

• Pyrethroids are bioconcentrated by fish

• Pyrethroids are bioconcentrated by birds

• Pyrethroids are bioconcentrated by mammals

• Pyrethroids are bioconcentrated by plants

• Pyrethroids are bioconcentrated by fungi

• Pyrethroids are bioconcentrated by bacteria

• Pyrethroids are bioconcentrated by protists

• Pyrethroids are bioconcentrated by viruses

• Pyrethroids are bioconcentrated by microalgae

• Pyrethroids are bioconcentrated by macroalgae

• Pyrethroids are bioconcentrated by phytoplankton

• Pyrethroids are bioconcentrated by bacteria

• Pyrethroids are bioconcentrated by protists

• Pyrethroids are bioconcentrated by fungi

• Pyrethroids are bioconcentrated by plants

• Pyrethroids are bioconcentrated by animals

• Pyrethroids are bioconcentrated by humans

Pyrethroid aquatic risk assessment issues

- bioavailability -
 - dissolved organic matter?
 - sediment characteristics?
 - organic carbon characteristics?
 - measurement – selective methods,
e.g. SPME

Pyrethroid aquatic risk assessment issues

- bioavailability
- co-occurrence common-additive toxicity - universal?
Type I + Type II?

Pyrethroid aquatic risk assessment issues

- bioavailability
- co-occurrence and additive toxicity
- chirality - stereoisomeric selectivity in toxicity
=> biological degradation?

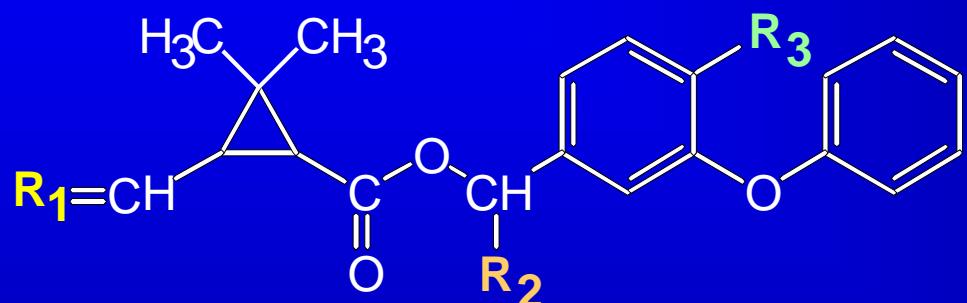
Pyrethroid aquatic risk assessment issues

- bioavailability
- additive toxicity - universal? Type I + Type II?
- chirality - selectivity: toxicity, degradation
- mechanisms of off-site movement in urban environment?
principal contributing uses?

Pyrethroid aquatic risk assessment issues

- bioavailability
- additive toxicity - universal? Type I + Type II?
- chirality - selectivity in toxicity, degradation
- urban off-site movement mechanisms?
- synergist co-occurrence?
PBO, MGK-264 (*N*-octyl bicycloheptene dicarboximide)

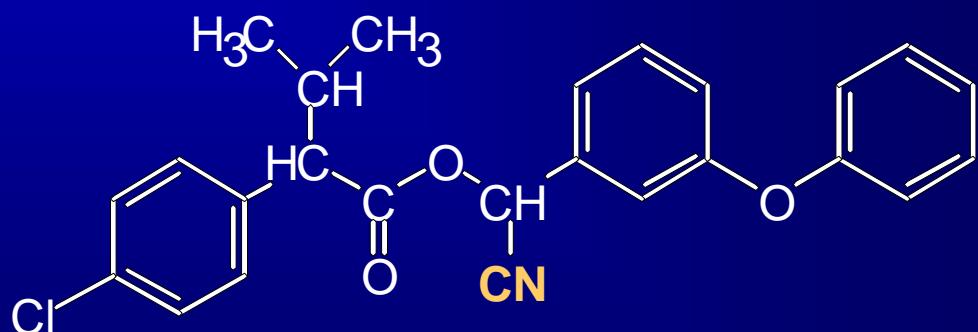
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